

UCRL- 96132
PREPRINT

CIRCULATION COPY
SUBJECT TO RECALL
IN TWO WEEKS

THE POTENTIOMETRIC TITRATION OF MERCURY
IN MERCURIC CYANIDE

Walter S. Selig

This paper was prepared for submittal to
Zeitschrift für Analytische Chemie

February 1987

Lawrence
Livermore
National
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

The Potentiometric Titration of Mercury in Mercuric Cyanide*

Walter S. Selig

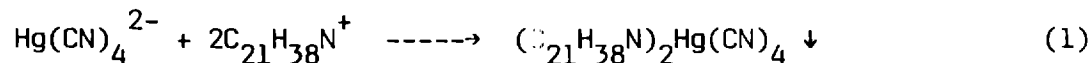
Lawrence Livermore National Laboratory
University of California
P. O. Box 808
Livermore, CA 94550

Summary

Mercuric ion in mercuric cyanide can be determined by potentiometric titration with iodide in 1.8 to 2.4 M nitric acid. In the presence of small amounts of ferric ion, a 1 M nitric acid medium is sufficient. The titration is monitored with an iodide ion-selective electrode (ISE) and a double-junction reference electrode.

Introduction

We have previously determined mercuric cyanide by converting it with an excess of cyanide to the tetracyano complex, and then titrating the latter potentiometrically with cetylpyridinium chloride, according to the reaction [5]:



In order to avoid using a large amount of potassium cyanide we have modified the method of Overman [2]. In this method mercuric ion is titrated potentiometrically with iodide according to the reaction



after the mercuric ion is released from the cyanide complex by addition of nitric acid.

* Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

Experimental

The indicating electrode was an Orion 94-53A iodide ISE; the reference was a double-junction Ag/AgCl electrode (Orion 90-01) with a 0.1 N sodium nitrate salt bridge. The titration system was controlled by a Tektronix 4051 graphics computer system which has been described previously [4]. Titration rates were kept constant at 0.3 ml/min. Stirring was provided by a magnetic stirrer. The stirring motor was isolated from the titration vessel by a water cooling plate and by a grounded aluminum plate. Titrations were performed at $23 \pm 1^\circ\text{C}$.

The titrant was 0.01 N or 0.05 N aqueous sodium iodide, standardized against high-purity potassium bromide. Note that reagent grade sodium iodide will, on long standing, form the dihydrate, and cannot be used as a primary standard without drying.

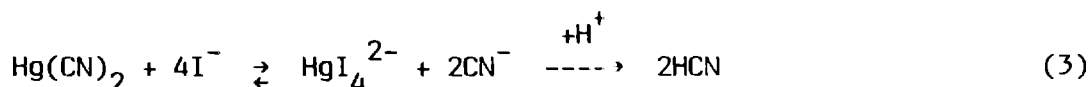
Recommended Procedures

For 1 to 10 mg of mercuric ion (as the cyanide) use the 0.01 N titrant; for larger amounts use the 0.05 N titrant. Weigh the sample, or deliver an aliquot by pipet, into a 50-ml beaker containing a Teflon-coated stirring bar. Add 7.5 to 10 ml of 6 N nitric acid and dilute to 25 ml with deionized water. Do the addition of acid and the subsequent titration in a well-ventilated hood. Titrate potentiometrically using an iodide ISE and a double-junction reference electrode.

If organic material is present, a wet oxidation of the material with nitric acid may be required. In this case add 0.5 to 1 g of sulfamic acid to each sample in order to remove oxides of nitrogen.

Results and Discussion

Mercuric cyanide is so weakly dissociated in aqueous solution that it fails to give the typical reactions for mercuric and cyanide ions. Despite this stability, however, an excess of iodide will liberate sufficient cyanide to be detected by addition of acid, according to the reaction [1]



The so-called Rupp method [3] is a redox method recommended by Kolthoff and Elving [1] for the determination of mercuric cyanide. The divalent mercury is reduced to metallic mercury with formaldehyde, followed by an iodometric titration. This is a "time-honored method capable of consistent accuracy, but only in the hands of an experienced analyst [1]". We have, therefore, previously converted mercuric cyanide to its tetracyano complex and titrated the latter with cetylpyridinium chloride [5] according to equation (1). However, because this method required handling fair amounts of potassium cyanide, we decided to modify the

method of Overman [2]. In this procedure mercuric ion is titrated with iodide, using an iodide ISE. This method can easily be adapted to the microscale and works in aqueous solution and in 0.1 N nitric acid. For mercuric cyanide, however, a more acidic medium is required. Optimum results were obtained in 1.8 to 2.4 M nitric acid solutions, or solutions containing between 45 and 60 mmol of nitric acid per 25 ml of solution. Ferric ion decomplexes some of the mercuric cyanide; in the presence of 0.2 mmol of ferric solution per 25 ml, the acidity may be reduced to 1 M nitric acid for satisfactory results. After acidification with nitric acid the solutions may be immediately titrated; no heating or waiting is required for removal of the hydrogen cyanide. However, acidification and titration of the samples should be carried out in a well-ventilated hood.

If solutions are heated with nitric acid in order to digest organic material, it is then mandatory to remove the oxides of nitrogen with sulfamic acid because these oxides will interfere in the titration with iodide.

Using 0.01 M sodium iodide as titrant, the endpoint breaks are several hundred mV. The relative percentage standard deviation for the normality of a typical titrant solution was 0.31% (4 replicates). A typical sample analysis yielded a mean value of 32.23% mercuric ion with a standard deviation of 0.08% for 4 replicates.

References

1. Kolthoff IM, Elving PJ Treatise on Analytical Chemistry (1961) Part II, Vol 3. New York: Wiley. 233-317.
2. Overman RF (1971) Anal Chem 43:616
3. Rupp E (1906) Arch Pharm 244:536; (1906) Ber Dtsch Chem Ges 39:3702; (1907) Ber Dtsch Chem Ges 40:3276
4. Selig W (1978 II) Mikrochim Acta 75
5. Selig WS (1984 II) Mikrochim Acta 455

1627L